Interfacial Processes in EES Systems Advanced Diagnostics

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2018 Annual Merit Review

June 18-21, 2018

Project ID# BAT085

Overview

Timeline

- This project was recompeted in FY15 and renewed in FY16 as part of Ni-rich high-voltage cathode project.
- This project is 70% complete

Barriers Addressed

- Inadequate Li-ion battery energy and power density, and calendar/cycle lifetimes for PHV and EV applications
- High cell/electrode/interface impedance that limits power and affects system safety

Budget

- FY18 funding $440K
- FY17 funding $440K
- FY16 funding $440K

Partners

- ABMR Cathode and Anode Task Groups
  - ANL, LBNL, SUNY, UP, HQ, NREL, URI, UM and UU
  - G. Chen, V. Battaglia, M. Doeff, K. Persson, V. Zorba, W. Yang,C. Martin, C. Ban, B. McCloskey
  - ALS, H. Bechtel, E. Rotenberg, E . Crumlin
- NTU (Singapore), M. Srinvasan
- UCL (UK), P. Shearing
- Umicore, Farasis Energy, Inc.

Relevance: Objectives

1. Develop advanced experimental methodologies to study and understand the mechanism of operation and degradation of high capacity materials for rechargeable cells for PHEV and EV applications.

2. Apply *in situ* and *ex situ* far- and near-field optical multifunctional probes to obtain detailed insight into the active material structure and the physio-chemical phenomena at electrode/electrolyte interfaces at a spatial resolution that corresponds to the size of basic chemical or structural building blocks.

3. Design new diagnostic techniques and experimental methodologies that are capable to unveil the structure and reactivity at hidden or buried interfaces and interphases that determine material, composite electrode and full cell electrochemical performance and failure modes.

Milestones

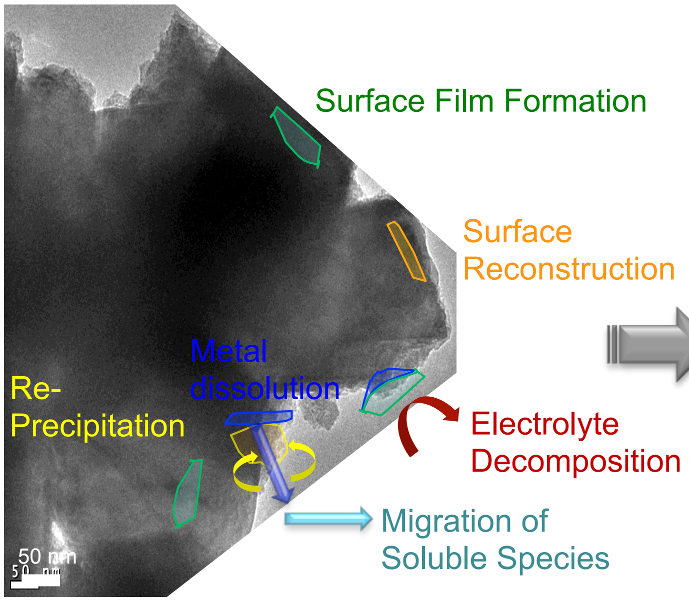
1. Controlled growth of model thin film electrodes by pulsed laser deposition (PLD) as model system for fundamental electrochemical studies. Go/No-Go Criteria: Stoichiometric thin films produced with sub nanometer roughness (December 2017 – complete)
2. Characterize the bulk and surface structure of model PLD thin films and its relation to electrochemical properties. Go/No-Go Criteria: Electrochemical performance of model system in line with that of bulk materials. (March 2018 – complete)
3. Characterize the chemistry of electrolyte decomposition at model PLD thin film electrodes with near field technique. (June 2018 – complete)
4. Determine the electrochemical impedance contribution from the interface between organic electrolyte and electrode active material. Go/No-Go Criteria: Development of model electrodes with high electrochemical stability and low impedance. (Q4 status - on schedule)

Approach

- Develop, apply and couple advanced characterization techniques, such as optical (Raman, ATR-FTIR) and scanning probe spectroscopy and microscopy (near-filed IR) with standard electrochemical methods to determine function, operation and degradation of materials, electrodes and battery cells.
- Construct ultra-smooth, defined model cathodes by pulsed laser deposition (PLD) to permit the use of novel investigative techniques during operation.
    - Study interfacial reactions and organic film formation between organic electrolytes and Ni-rich NMC.
    - Obtain detailed insights into the organic film composition, distribution and contribution on impedance in Ni-rich NMC cathodes.

Interfacial Reactivity of NMC

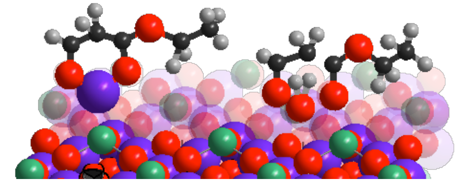
Multiple processes take place at the electrode-electrolyte interface, which can contribute to the observed impedance increase and electrode degradation



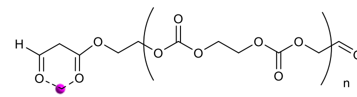
Adapted from J. Vetter, et al,, *J. Power Sources*, 2005, **147**, 269-281

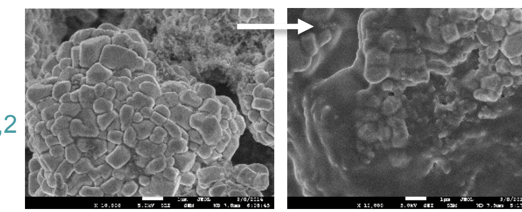
1. Electrolyte Decomposition[1]

2. Metal Dissolution[1]

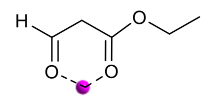


3. Fluorescent Surface Film Formation[1-5]

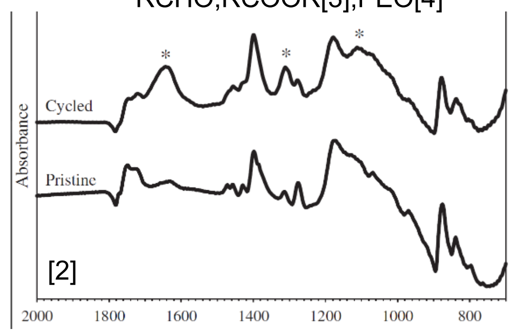


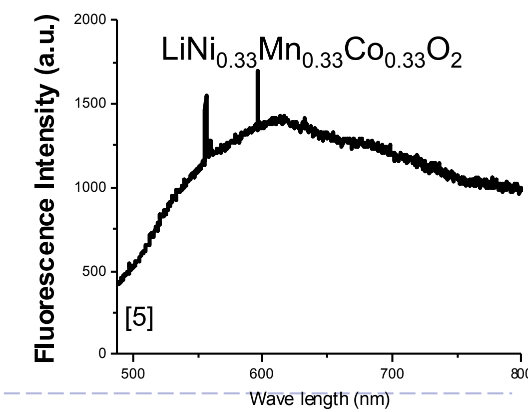


4. Migration of Soluble Species[1,2]

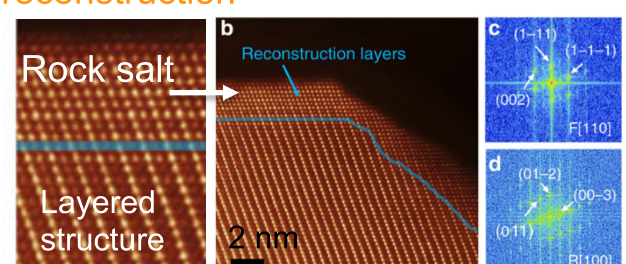


* Carbonyl groups: RCHO,RCOOR[3],PEO[4]



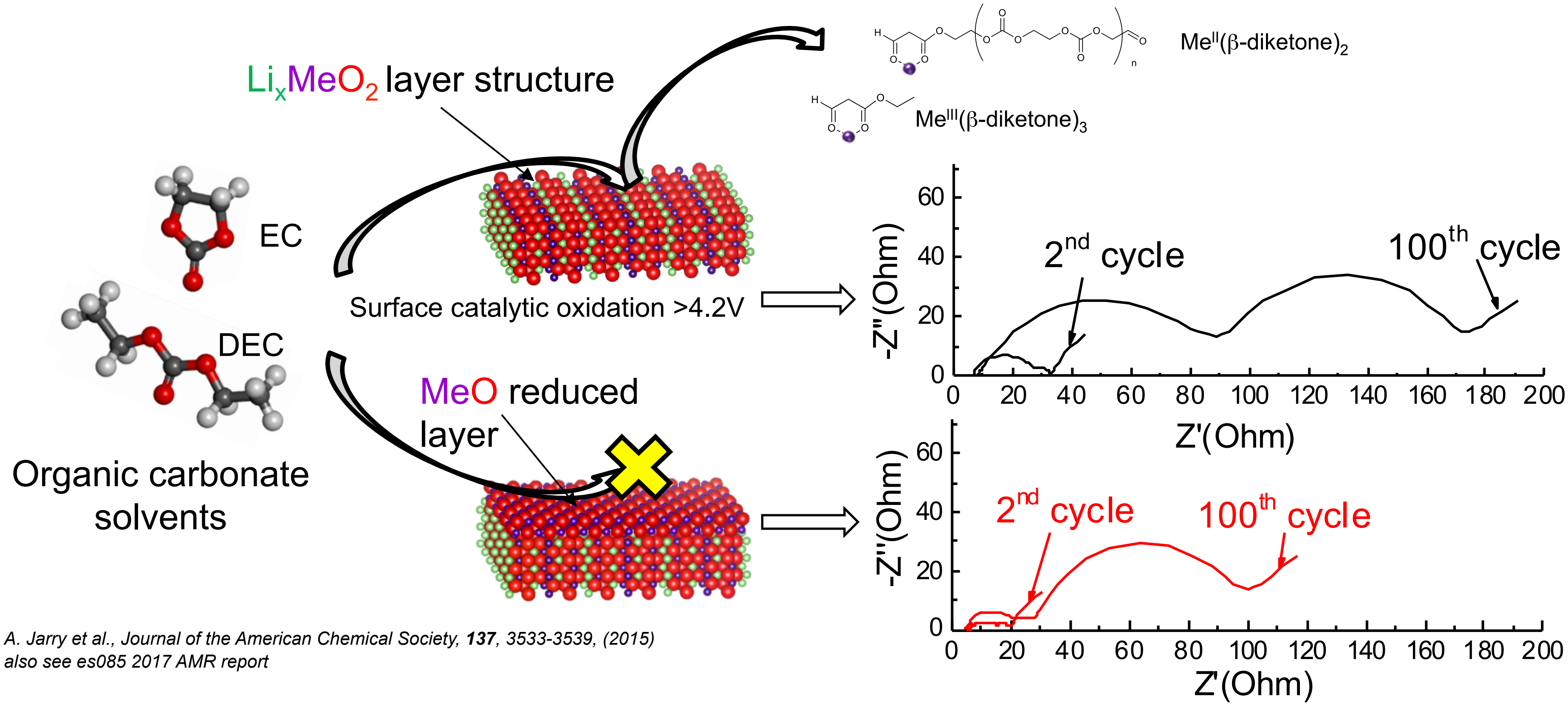


5. Surface reconstruction[6]



1. *A. Jarry et al., JACS, **137**, 3533-3539, (2015).*
2. *N. S. Norberg et al.,, Electrochem. Commun. 34, 29-32, (2013)*
3. *M. Moshkovich et al.,, J. Electroanal. Chem., **497**, 84, (2001)*
4. *S. E. Sloop et al., J. Power Sources, **119–121**, 330-337, (2003)*
5. *2016 AMR report*
6. *Lin et al., Nat. Com., (2014)*

Origins of Interfacial Impedance Rise in NMC Cathodes

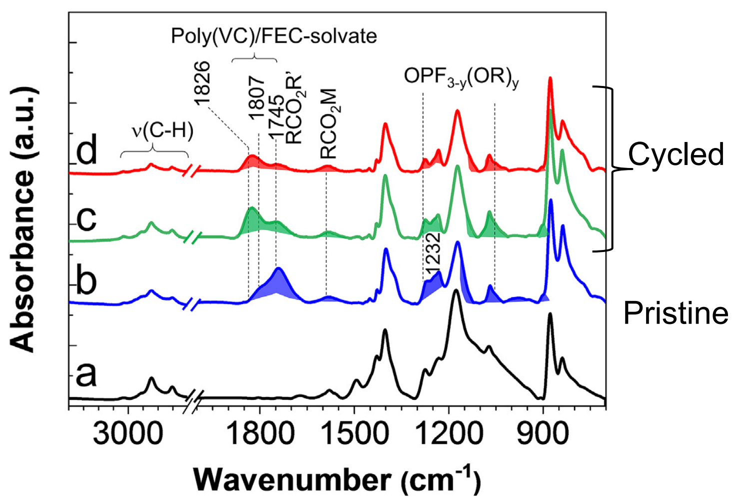


A. Jarry et al., Journal of the American Chemical Society, ***137****, 3533-3539, (2015)*
also see es085 2017 AMR report

- Electrolyte oxidation, Me dissolution and surface film formation during cycling are responsible for the observed impedance rise of NMC cathodes.
- $Me^{(II)}O$ surface sub-layer in NMC suppresses oxidation of the electrolyte, inhibits surface film formation, and suppresses impedance increase during cycling.

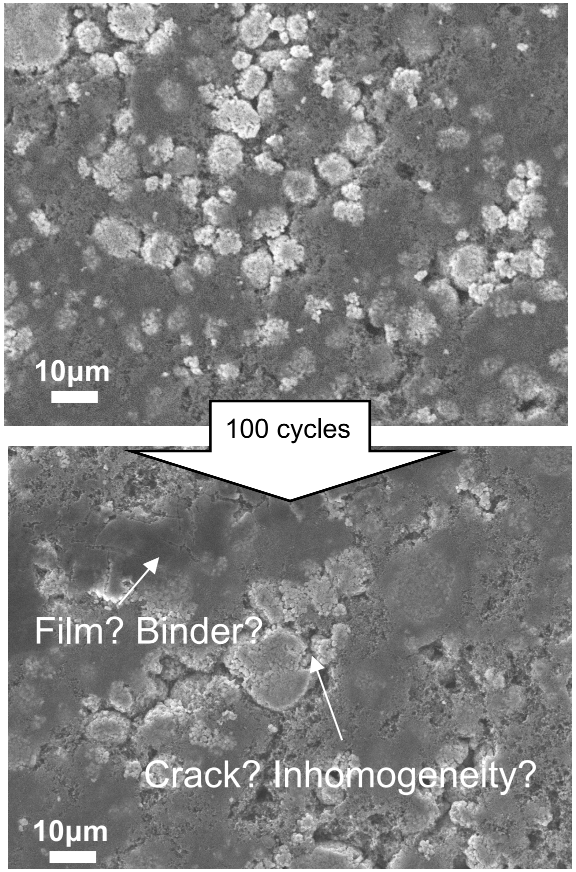
NMC Composite Cathodes: Characterization Challenges

ATR-FTIR of NMC532 composite electrodes

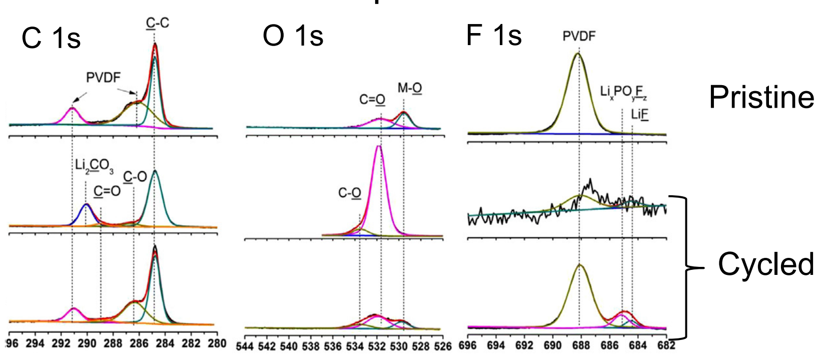


Nguyen et al., J. Power Sources, ***303****, 150 (2016).*

SEM of NMC532 composite electrodes



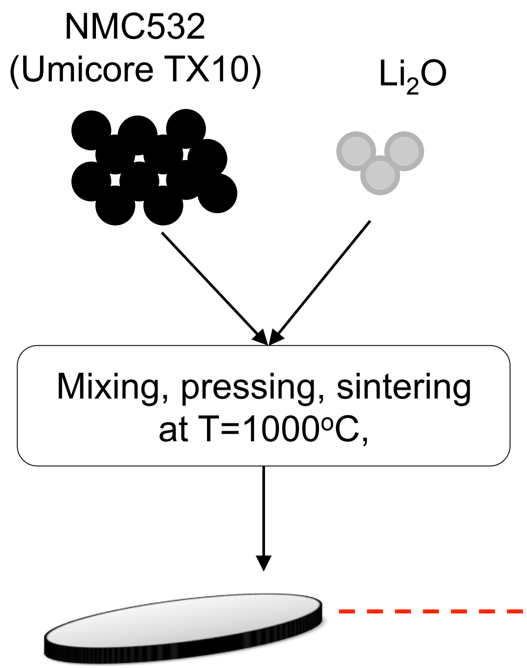
XPS of NMC111 composite electrodes



X. L. Liao et al., Electrochim. Acta, ***212****, 352 (2016)*

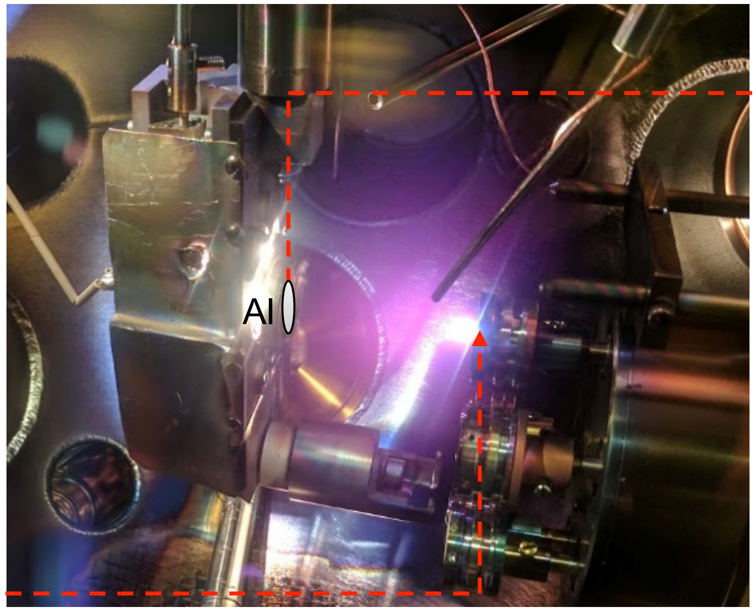
- Convoluted signals from active and passive composite electrode components.
- Multiple phenomena and processes at active and passive materials coincide and interfere with degradation of mechanical properties of the composite electrode.

Manufacturing Thin-Film NMC532 Model Electrodes



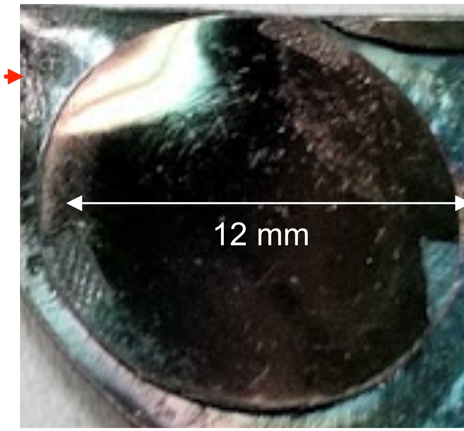
PLD target

Pulsed Laser Deposition System



O_2 pressure: 25-150 mTorr
Al-foil substrate
Substrate temperature: 600°C
Sample-target distance: 50 mm

NMC532 thin-film (200 nm)

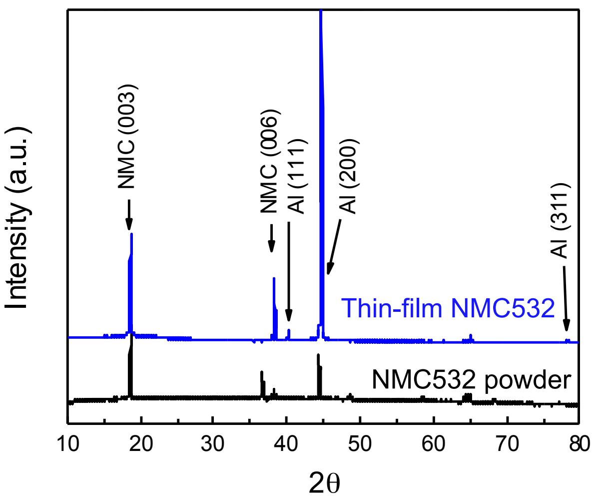


Pulsed Laser Deposition (PLD) was used to manufacture binder- and carbon-free thin-film NMC532 model electrodes.

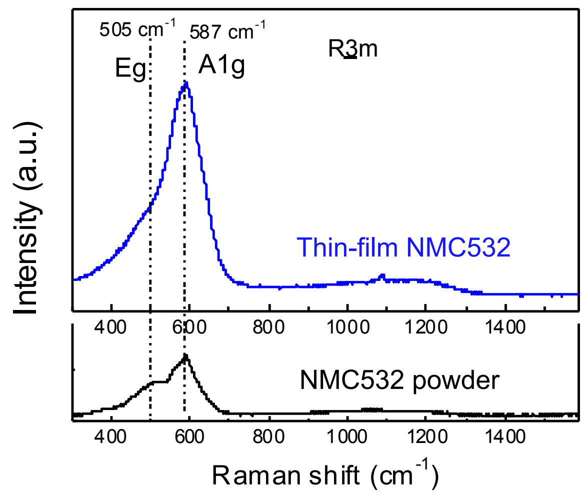
PLD samples prepared at UCB Materials Dept and Advanced Light Source by J. Franklin (Chem Eng, UCL)

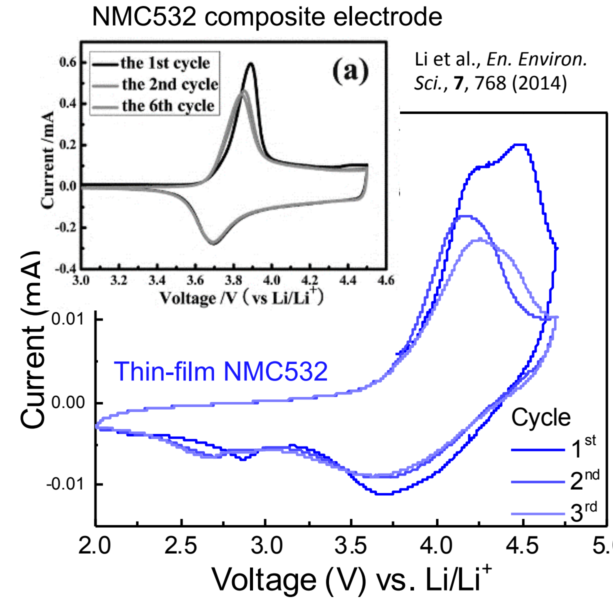
Characterization of Thin-Film NMC532 Model Electrodes

XRD



Raman spectroscopy



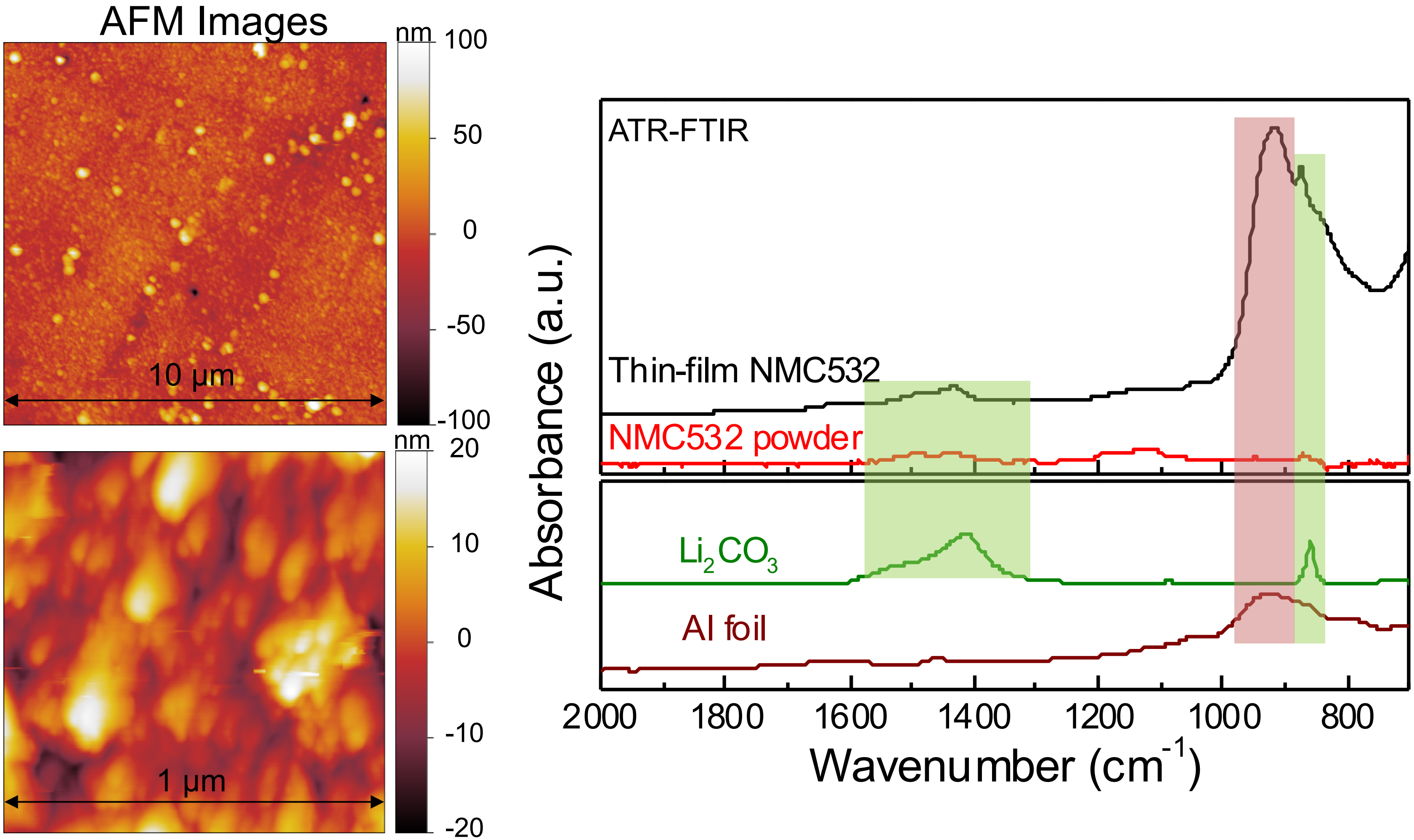


1.2 M $LiPF_6$ EC:DEC (1:2 wt.%)
Li anode, CVs: 2-4.7 V, v=0.2mV/s

- ICP-MS analysis of NMC thin-films confirms Ni:Mn:Co wt. ratio 5:3:2.
- X-ray diffractograms and Raman spectra of NMC532 thin-films reveal $R\bar{3}m$ layered structure with (003) preferred orientation.
- Cyclic voltammetry plots of the thin-film NMC532 electrode are similar to CVs of the analogous NMC 532 composite electrode.

Thin-film NMC532 model electrode exhibits similar properties/behavior as the commercial NMC532 powder.

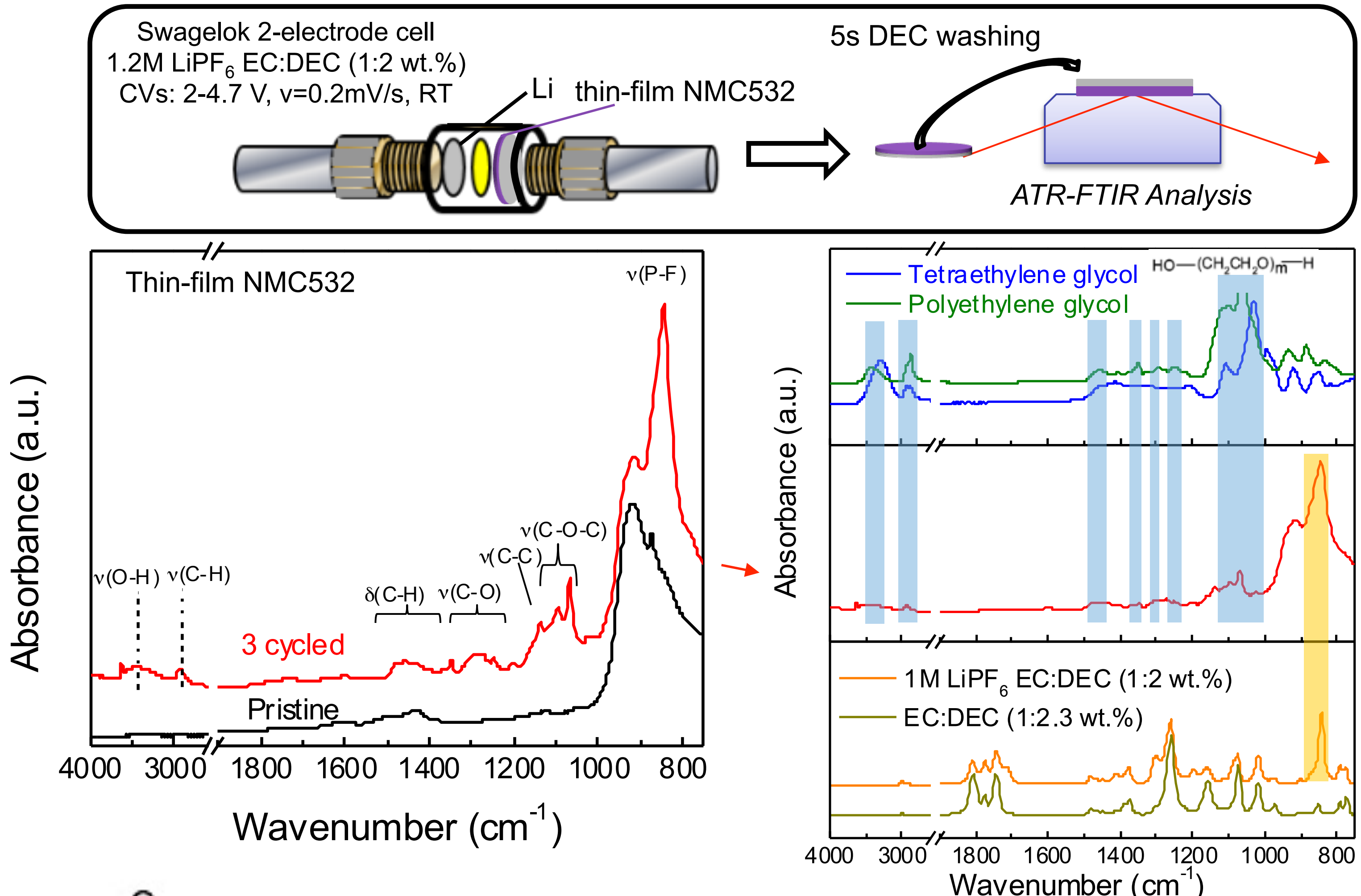
Surface Characterization of Pristine NMC532 Electrode

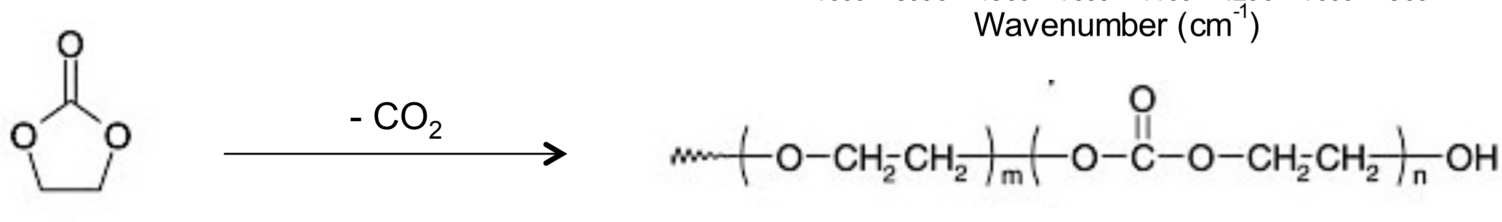


- 200 nm thick NMC532 electrode consists of closely packed 50-100 nm nanoparticles with RMS surface roughness ca. 5.8 nm.
- Traces of Li_2CO_3 detected on the surface.

Thin-film NMC532 electrode provides a well-defined and reliable experimental platform for fundamental interfacial studies.

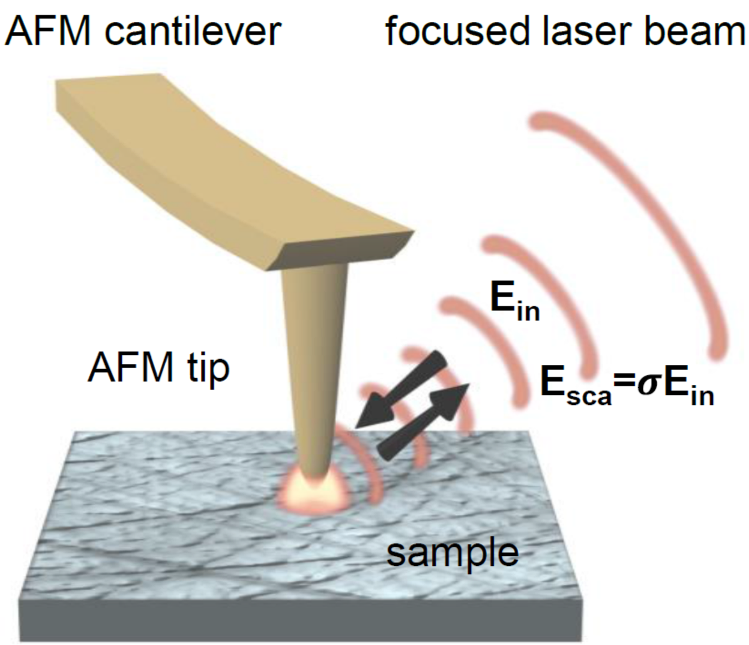
Ex situ ATR-FTIR Spectroscopy of Cycled NMC532 Electrode



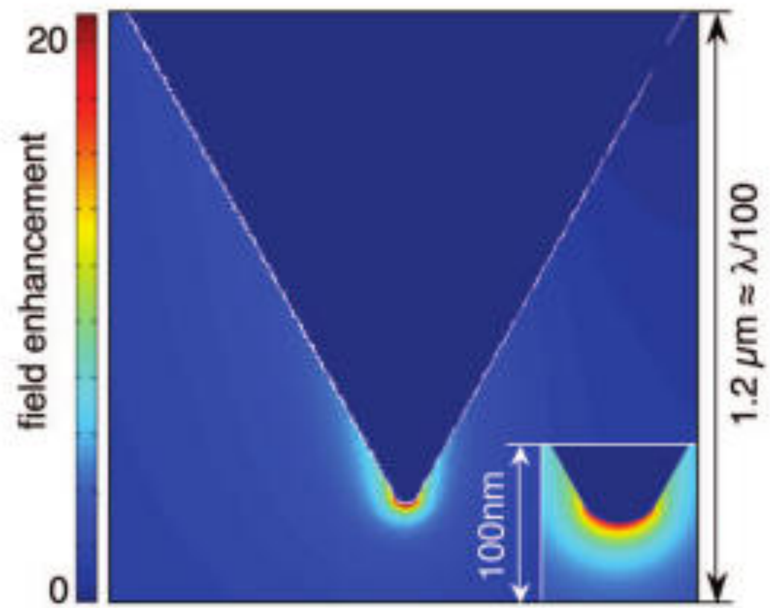


FTIR spectrum the NMC532 electrode after 3 cycles reveals features characteristic for polyethylene glycol and $LiPF_6$.

Apertureless Near-Field IR Microscopy/Spectroscopy



Ocelić, PhD thesis, TU Munich, (2007)



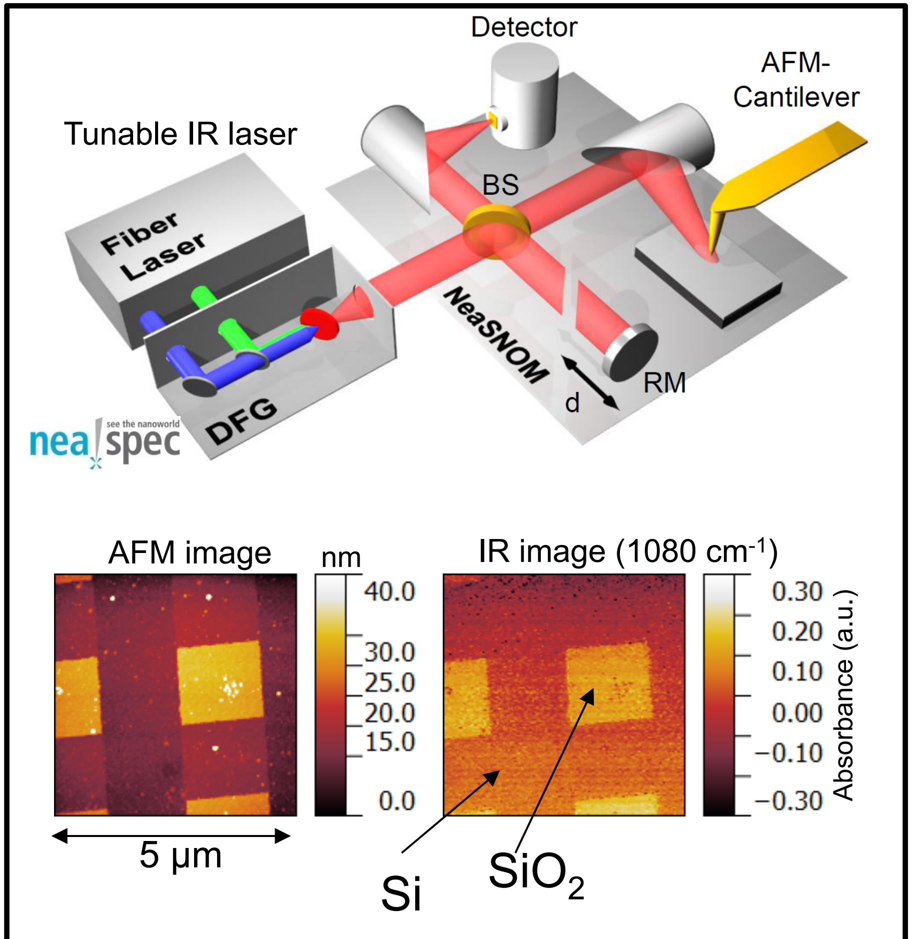
A. J. Huber et al., *Nano Lett.*, **8**, 3766 (2008)

- A focused laser-beam (E_{in}) illuminates a Me-coated AFM tip and induces a strong dipole at the tip apex.
- The tip nano-dipole induces a mirror-dipole in the sample (Lighting Rod Effect), which interacts with phonons in the material.

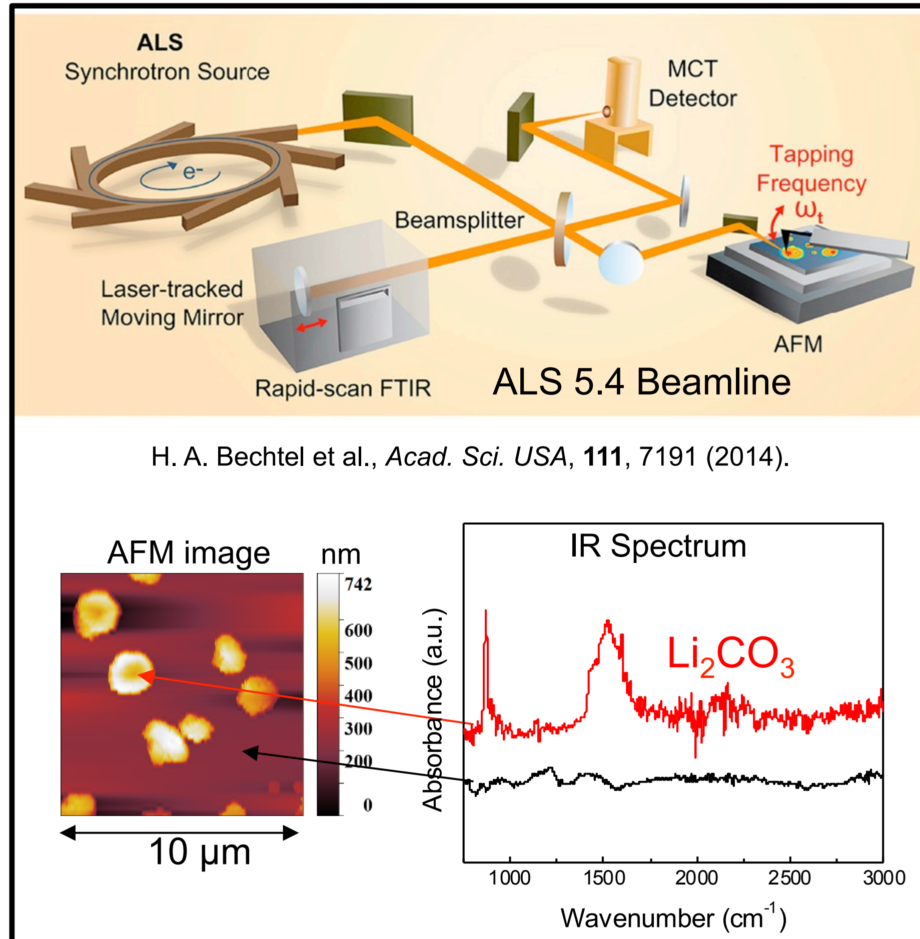
Apertureless Near-field IR microscope/spectroscopy has 10 nm spatial resolution, breaking the detection limit of spatial resolution > 1um of general far-field IR system.

Apertureless Near-Field IR Microscopy/Spectroscopy

Neaspec Scattering-type Scanning Near-field Optical Microscopy (NeaSNOM)



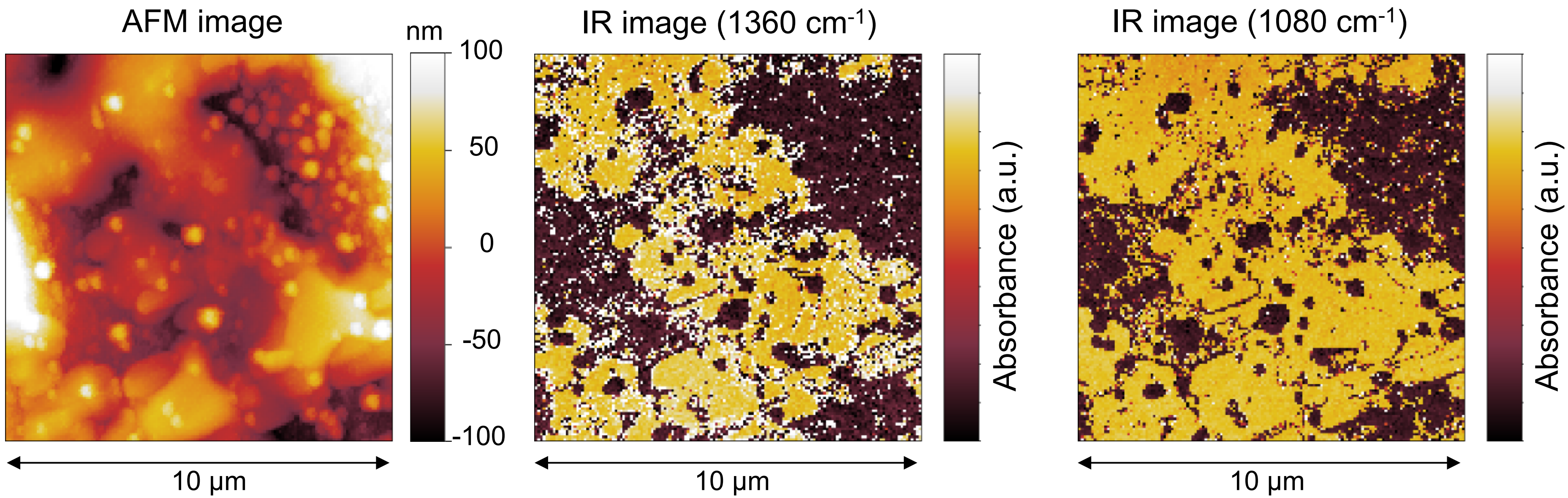
Synchrotron Infrared Nano Spectroscopy (SINS)



BMR Program and LBNL has been pioneering the development and use of IR SNOM techniques to study basic phenomena in energy storage systems.

IR NeaSNOM of Cycled Thin-Film NMC532 Electrodes

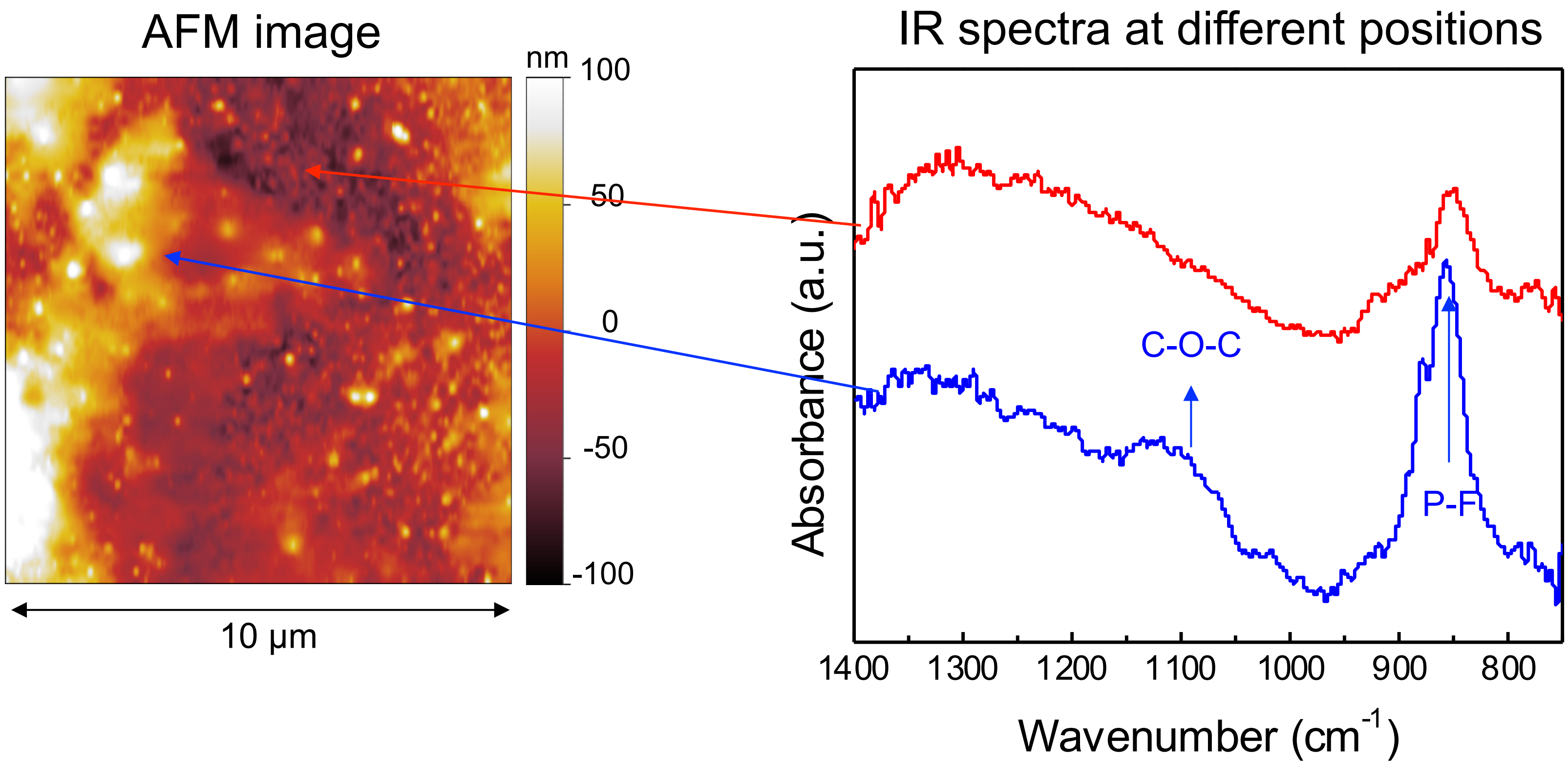
After 3 cycles electrode was washed in DEC for 5s



- AFM topography image of the thin-film NMC532 electrode after 3rd cycle displays a inhomogeneous cathode/electrolyte interphase (CEI) layer.
- IR NeaSNOM images of thin-film NMC532 electrode at 1360 cm^{-1} $v_{(C\text{-}O)}$ and 1080 cm^{-1} $v_{(C\text{-}O\text{-}C)}$ display a highly non-uniform distribution of chemical components.
- Polyethylene glycol compounds are distributed unevenly at the NMC532 surface.

SINS of Cycled Thin-Film NMC532 Electrode

After 3 cycles electrode was washed in DEC for 5s



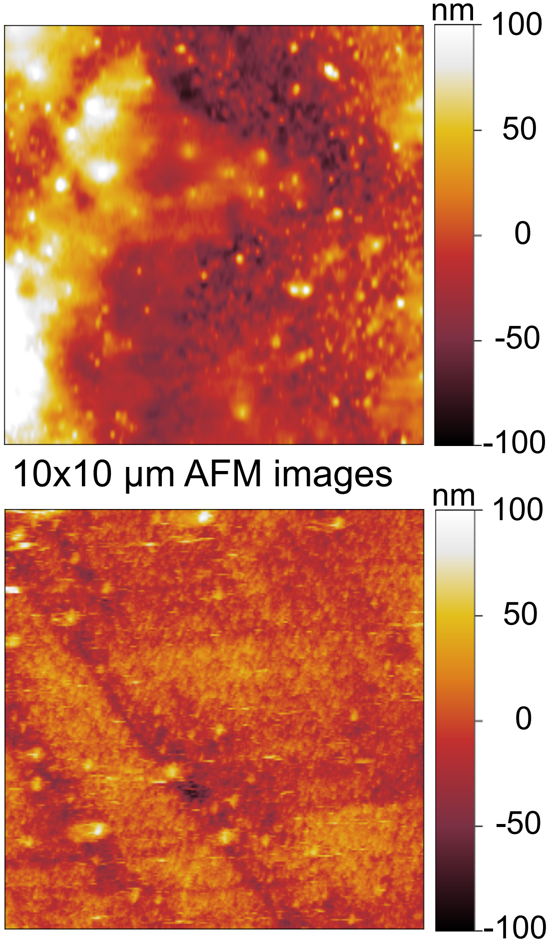
- SINS analysis of the outer layer shows a broad IR adsorption band at ca. 1080 cm^{-1} $v_{(C\text{-}O\text{-}C)}$, which can be attributed to polyethylene glycol.
- IR $v_{(P\text{-}F)}$ mode at 950 cm^{-1} is observed at all locations.

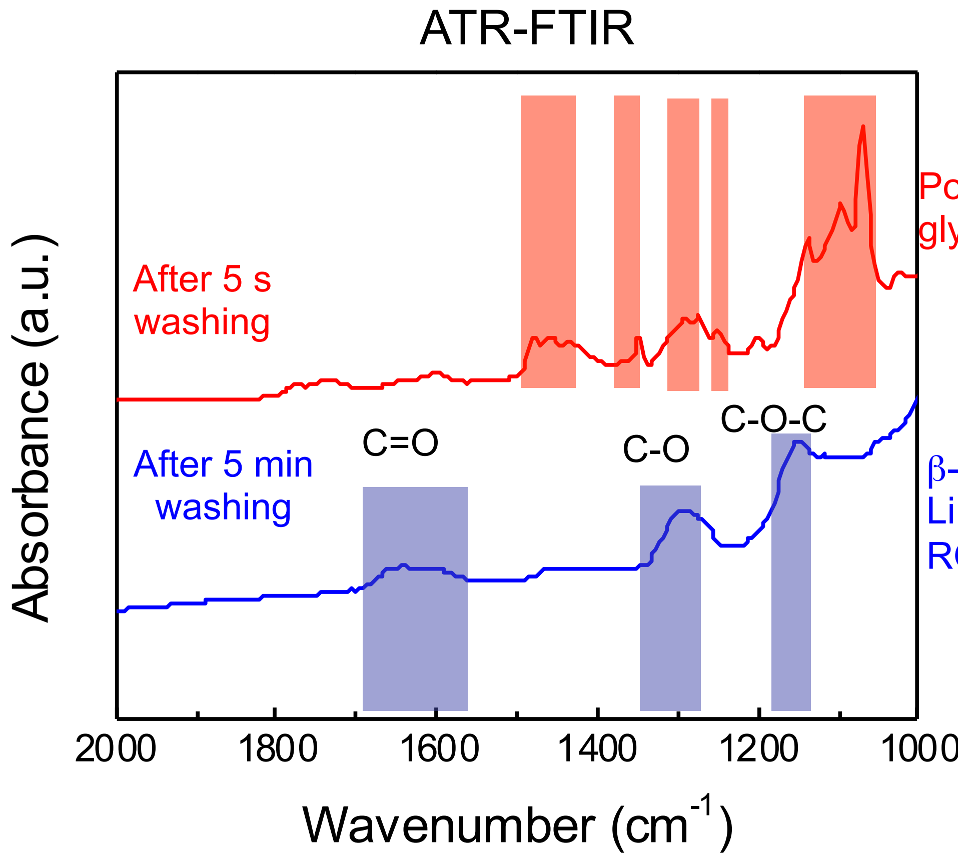
Collaboration with H. Bechtel, ALS/LBNL

Stratified Structure and Chemical Composition of the CEI at NMC532 Electrode

After 5 s washing

After 5 min washing

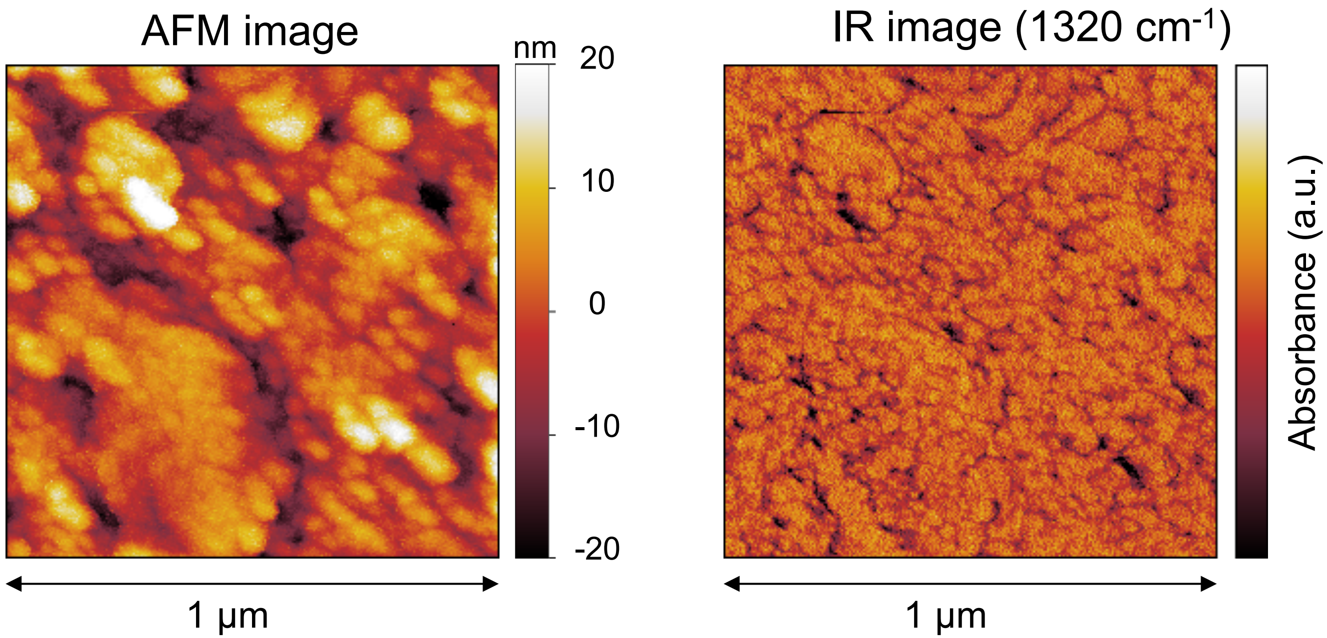




- Prolonged washing in DEC selectively removes the outer layer.
- ATR-FTIR spectra of the inner and outer layer correspond to $ROCO_2Li$, ROLi and β-diketone species, and polyethylene glycol, respectively.

IR NeaSNOM of Cycled Thin-Film NMC Electrode

After 3 cycles electrode was washed in DEC for 5s

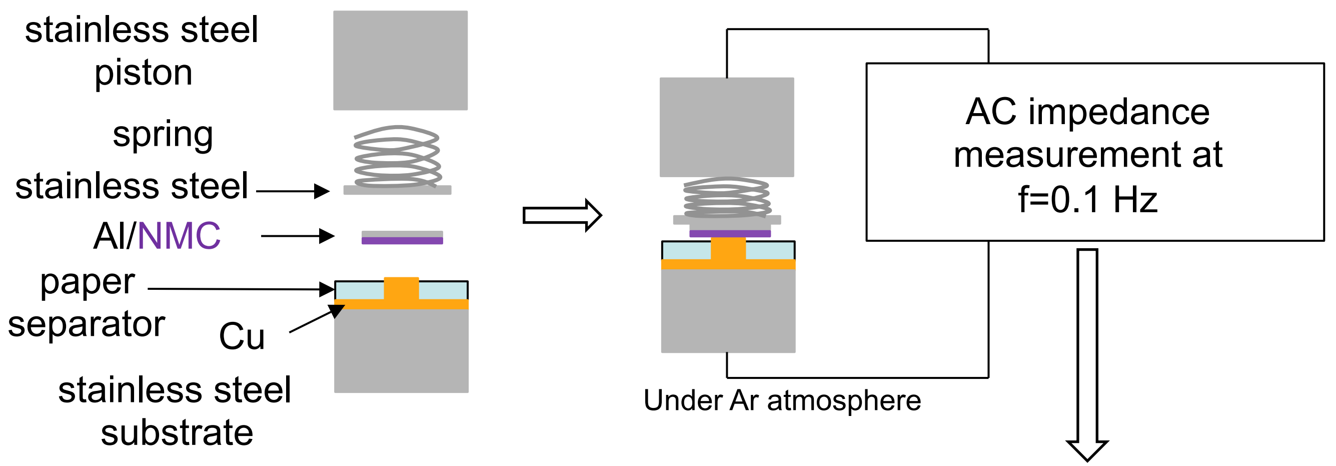


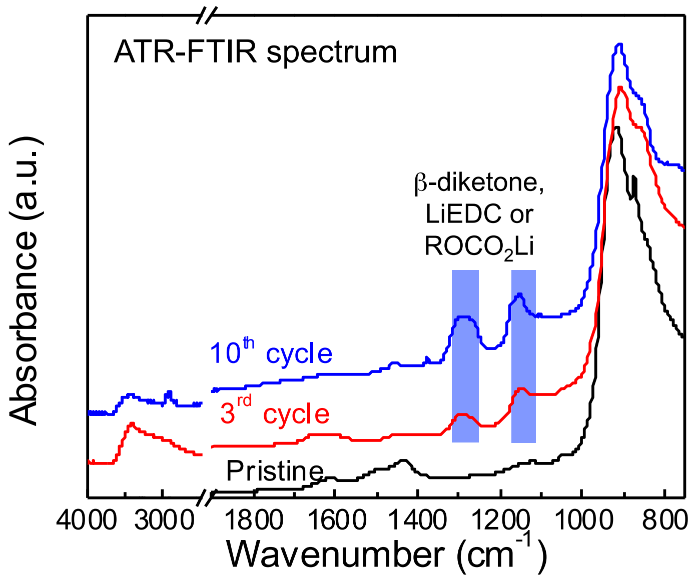
- AFM image of thin-film NMC532 after 3rd cycle and 5 min washing in DEC presents similar morphology of the pristine NMC532 surface.
- IR NeaSNOM image of thin-film NMC 532 at 1320 cm^{-1} $v_{(C\text{-}O)}$ suggests a uniform chemical composition.

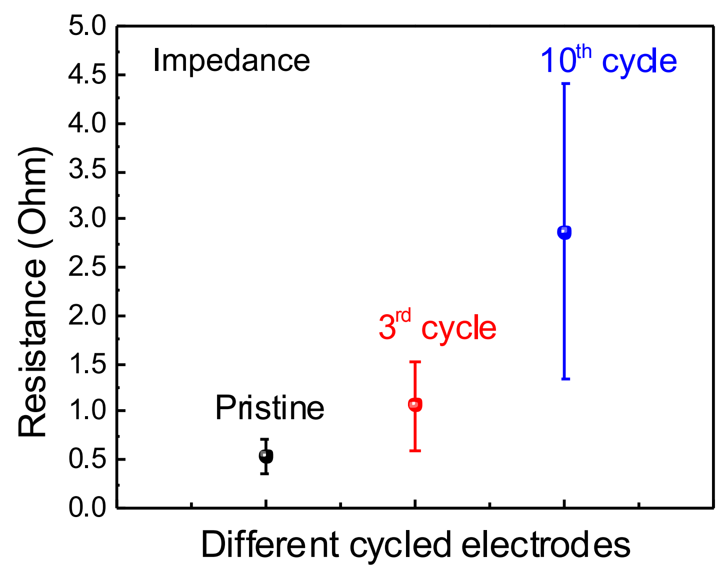
$ROCO_2Li$, ROLi and β-diketone species, which formed on NMC due to nucleophilic reactions between NMC and EC or DMC homogeneously cover the surface of thin-film NMC532 electrode.

Ex situ Impedance Analysis of Cycled NMC532 Electrodes

Cycled electrodes were washed in DEC for 5 min

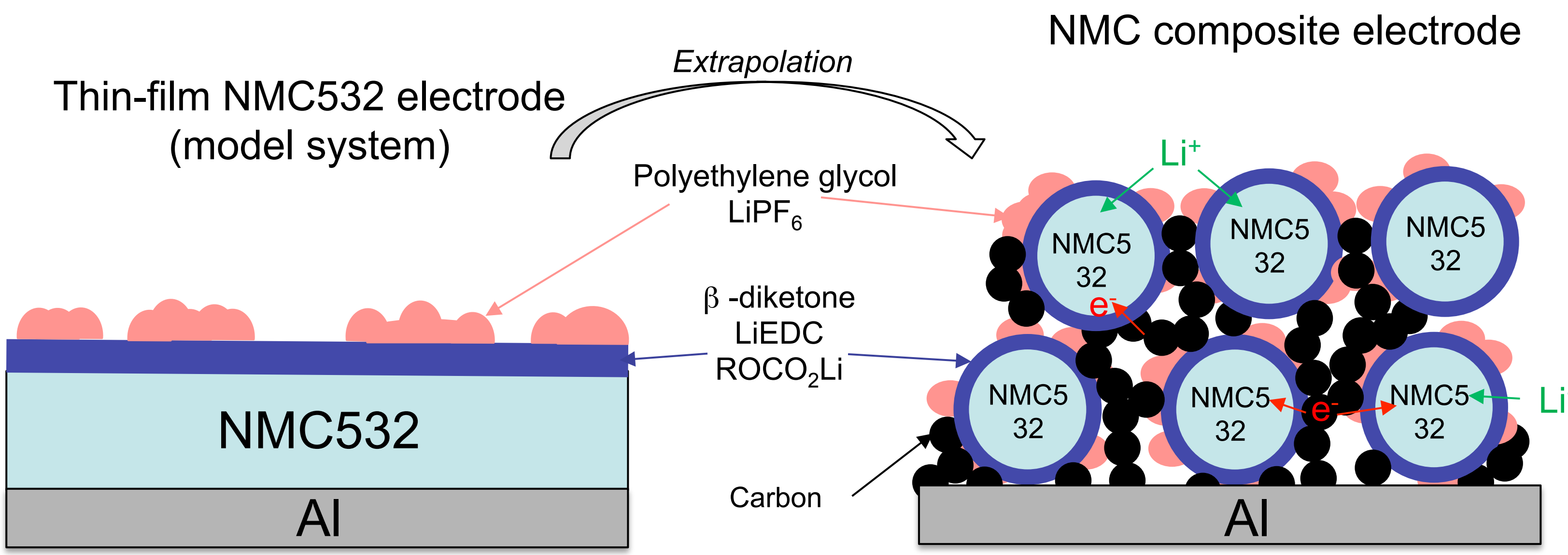






The observed impedance rise correlates with the thickness increase of the CEI inner layer ($ROCO_2Li$, ROLi and β-diketones) upon cycling.

Schematic Diagram of the CEI Film on NMC Electrode



- We anticipate that the non-uniform polyethylene glycol has a minor to moderate effect on the NMC composite electrode impedance. In fact, enhanced Li^+ transport in polyethylene glycol-based gel electrolytes was previously observed.
- However, the continuous and uniform inner layer of β-diketones, LiEDC and/or $ROCO_2Li$ can form an effective barrier for electron and ion transport between NMC active material and electrolyte, carbon additives and/or Al current collector.

Summary

- Thin-film NMC532 model electrodes were successfully produced by Pulsed Laser Deposition. The model NMC532 electrode exhibits a similar structure, chemical composition and electrochemical properties as commercial NMC532 powder.
- Cathode electrolyte interphase (CEI) on the NMC532 model electrode after cycling exhibits a stratified composition and structure.
  - Polyethylene glycol-based outer CEI layer, which is distributed non-uniformly on the electrode surface may affect adversely contact resistances in the composite cathode. On the other hand it may enhance local Li-ion conductivity.
  - A uniform and dense inner CEI layer consists mainly of $ROCO_2Li$, ROLi and β-diketone species. It can form an effective barrier for charge and mass transfer at the electrode/electrolyte interface.
  - The increasing thickness of the CEI inner layer correlates with the electrode impedance rise during cycling.

This study not only determines the mechanism of the CEI layer film formation but also offers unique insight into its direct and indirect impact on the electrochemical performance and interrelated mechanism of interfacial phenomena at high-voltage NMC cathodes.

Remaining Challenges and Barriers

1. *The effect of NMC electrode composition (high Ni content) and surface structure on the electrode impedance has to be determined.*
2. *Understand the sequence, correlations and corresponding impact factors of different detrimental processes in the NMC cathode degradation mechanism.*
3. *The kinetic control over the interfacial side reactions has to be achieved via combined surface/electrolyte modification approaches.*

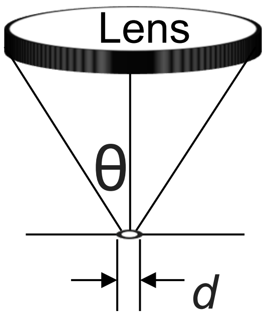
Future work

- Develop and apply Ni-rich NMC model systems of different compositions and advanced surface sensitive techniques to measure impedance distribution at each interface in battery system with different order of time or spatial scale.
- Quantify the effect of each the side reaction happened in electrolyte-electrode interface, including surface reconstruction, oxygen loss and transition metal dissolution, conductive carbon oxidation, Al current collector surface correction, and films formation at each electrolyte-solid interfaces during electrochemical cycling.
- Work closely with ABMR PIs and industry partners to establish clear connections between diagnostics, theory/modelling, materials synthesis, and cell development efforts.
- Develop and apply novel innovative experimental methodologies to study and understand the basic function and mechanism of operation of materials, composite electrodes, and Li-ion cells for PHEV and EV applications.

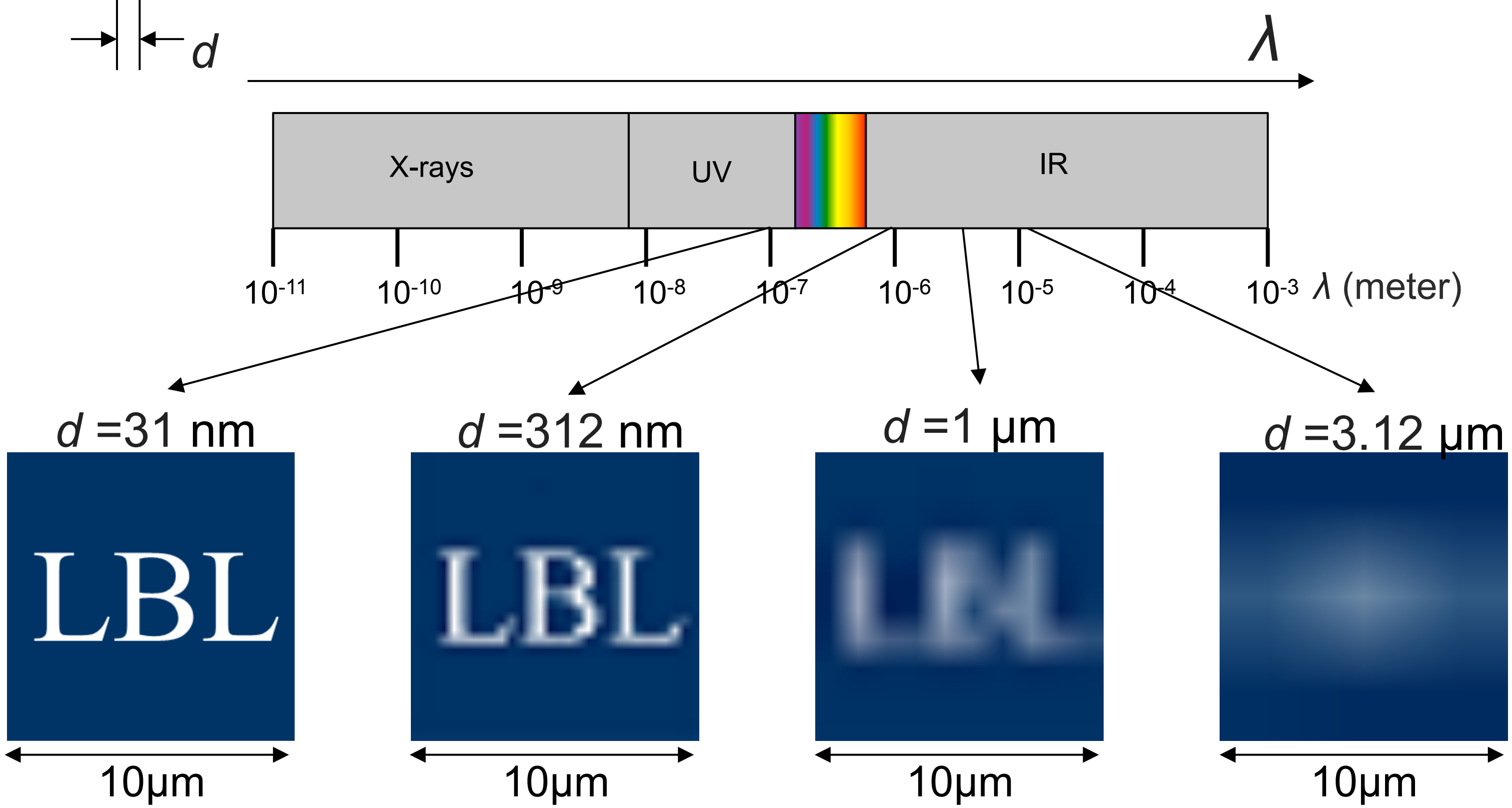
Any proposed future work is subject to change based on funding levels.

Technical Back-Up Slides

Limitations of Far-Field Microscopy/Spectroscopy



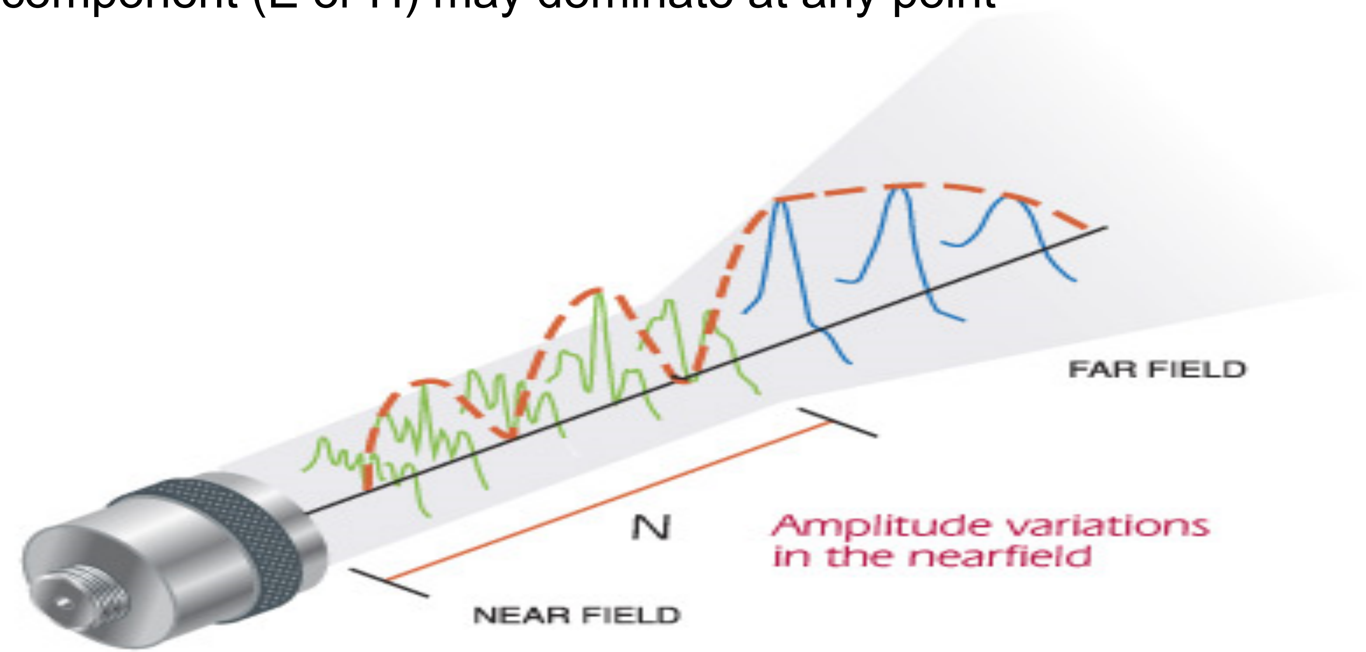
Abbe diffraction limit: $d = \lambda / 2n\sin(\theta) = \lambda / 2NA$
(for optical lens NA = 1.4–1.6, $d = \lambda/3.2$)



The spatial resolution of common far-field optical techniques is limited by the light wavelength

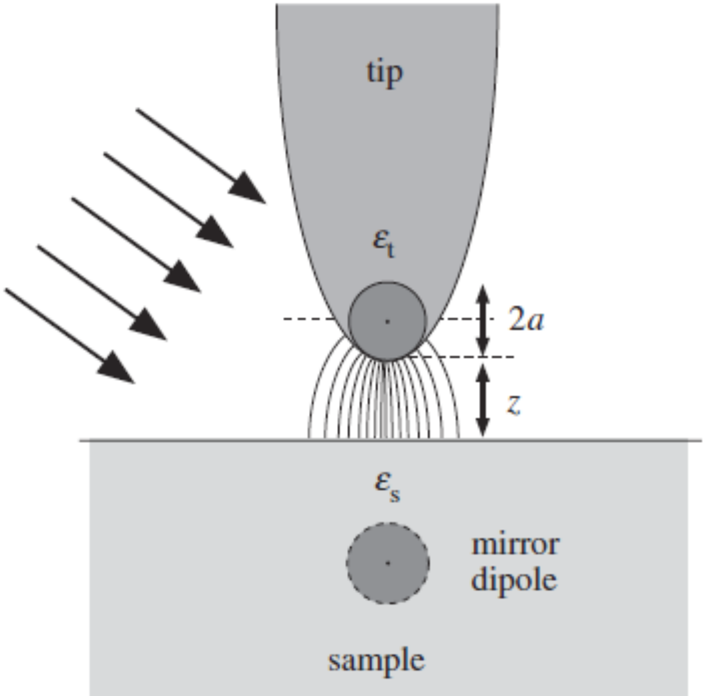
Far-Field vs. Near-Field Spectroscopy/Imaging

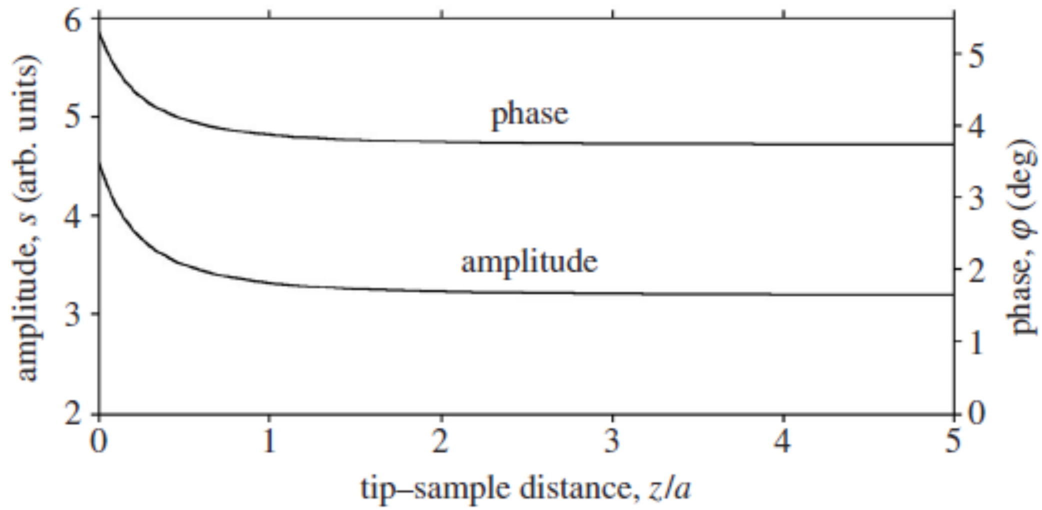
- Region extending farther than 2-3 wavelengths away from the source is called the *Far-Field*.
  - Relationship between the electric field component E and the magnetic component H is that characteristic of any freely propagating wave, where E is equal to H at any point in space
- Region located less than one wavelength from the source is called the *Near-Field*
  - Relationship between E and H becomes very complex, either field component (E or H) may dominate at any point



Apertureless Near-Field Probing

Theoretical background of near-field interaction



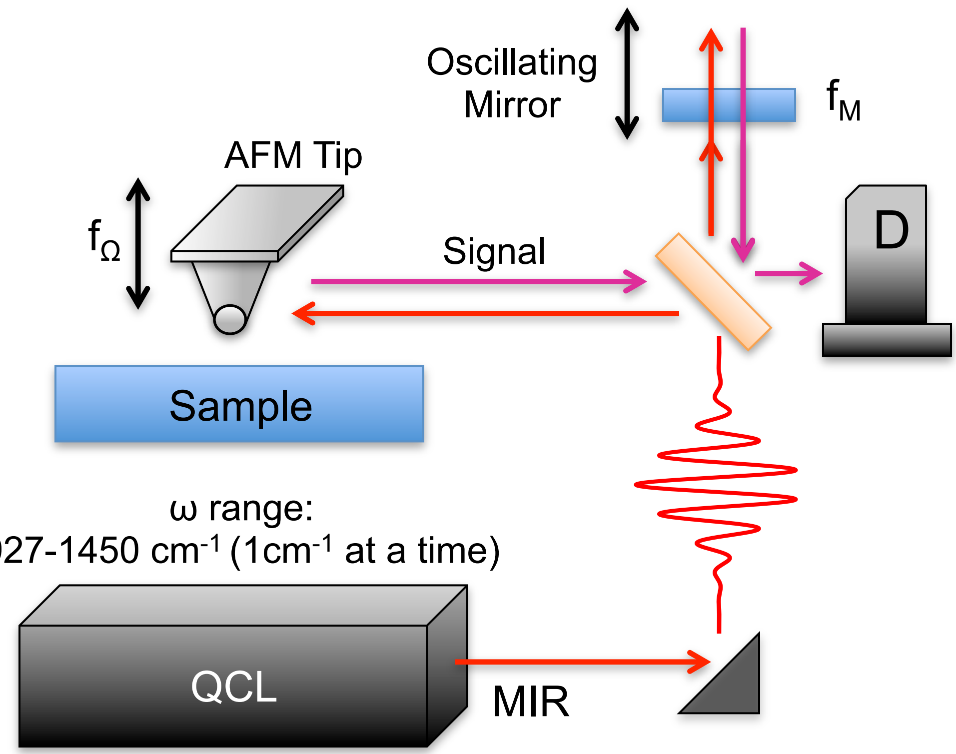


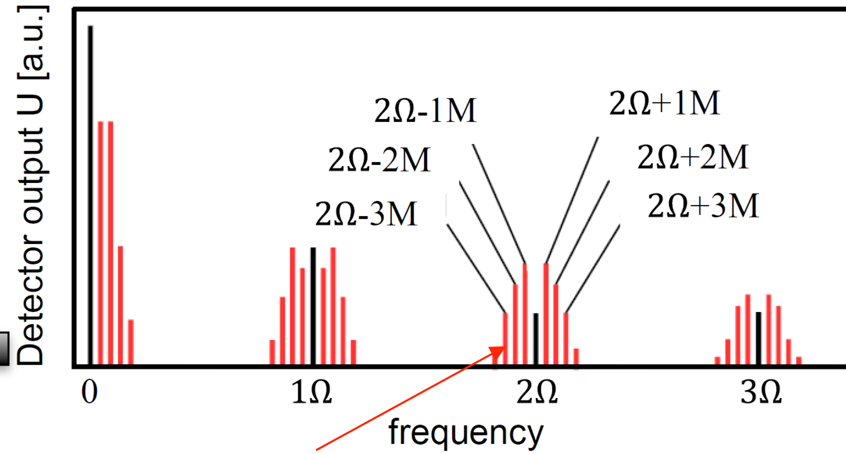
[1] Keilmann, Hillebrand, Phil. Trans. Royal Society 362(1817):787–805 (2004)

$$\alpha = 4\pi a^3 \frac{\boxed{\varepsilon_t} - 1}{\boxed{\varepsilon_t} + 2}, \qquad \beta = \frac{\boxed{\varepsilon_s} - 1}{\boxed{\varepsilon_s} + 1}, \qquad \alpha_{\text{eff}} = \frac{\alpha(1+\beta)}{1 - \alpha\beta/(16\pi(a + \boxed{z})^3)}.$$

- The nonlinear dependence $\alpha_{\text{eff}}(z)$ is used to eliminate unwanted ‘background’ scattering which generally dominates the detected signal.
- The focused laser beam illuminates a greater part of the tip shaft which typically extends 10μm from the cantilever, and also the sample.

Neaspec Scattering-type Scanning Near-Field Optical Microscopy (NeaSNOM)





Background free signal

U_{n1} (n Ω -1M), U_{n2} (n Ω -2M),…

n ≥ 2 for near field

S_n = 2.16 k

$_n$ = arctan

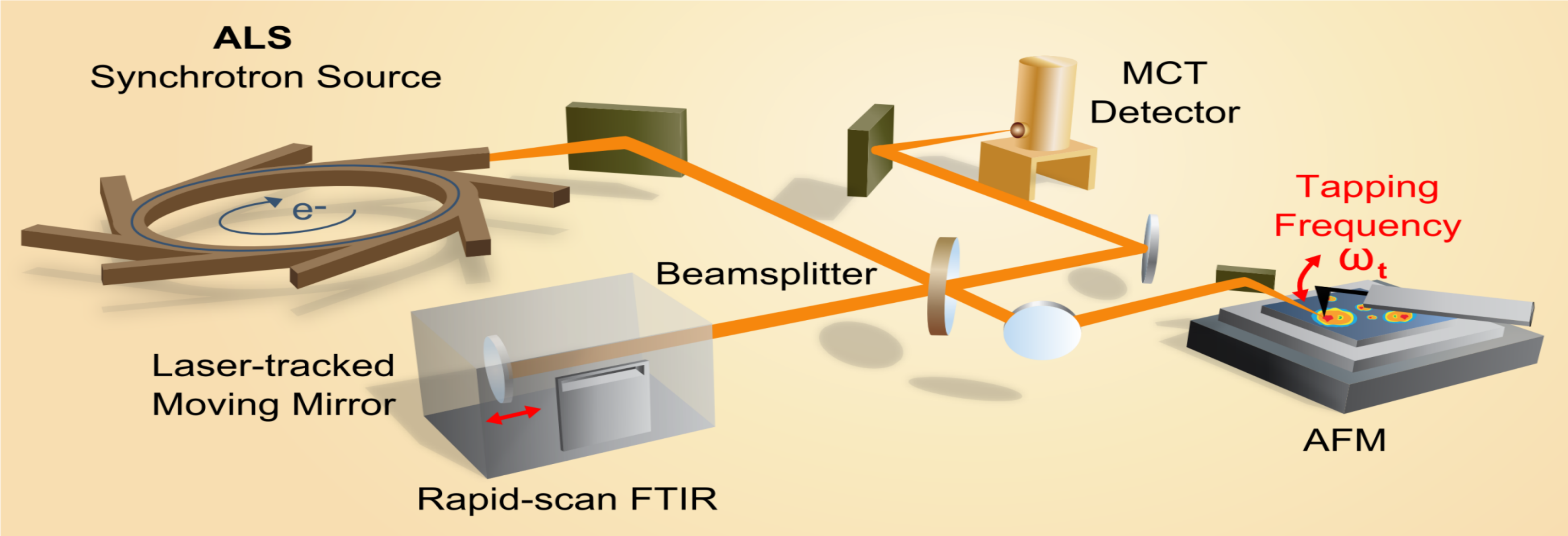
Laser beam focused on a vibrating mirror M (phase modulated reference beam at f_M = 300Hz) and on the oscillating AFM tip (f_W = 300KHz).

The demodulation of the detector output at a the side frequency *fn,m* = *n*W + *mM* provides the near-field signal amplitude (S_n) and phase (φ_n).

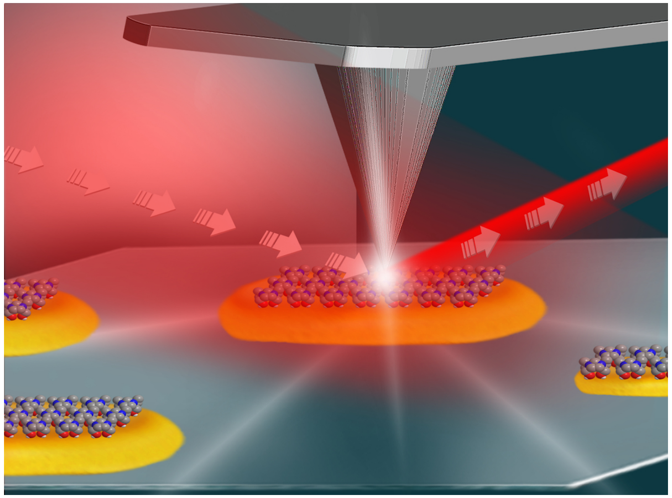
Background-free near field signal within an integration time of 6.5 ms (to 1.6 s) allowing fast raster scan imaging (~ 150 pixels / s).

LBNL ALS makes IR, too!

Near-Field Scanning Infrared Spectroscopy/Microscopy



Bechtel et al., PNAS, 111, 7191 (2014)



Using this synchrotron infrared nano-spectroscopy we achieve spectroscopic imaging with nanometer spatial resolution and high sensitivity that enables the investigation of nanoscale phenomena in energy storage model systems.

Collaboration and Coordination with Other Institutions

This work has been performed in close collaboration with:

- V. Battaglia: ABMR program leads
- ABMR Cathode and Anode Task Groups
    - ANL, LBNL, SUNY, UP, HQ, NREL and UU

    (R-C. Lee, J. Franklin, G. Chen, V. Battaglia, M. Doeff, K. Persson, V. Zorba, W. Yang, C. Ban, N. Balsara, B. McCloskey)
- Advanced Light Source (H. Bechtel, E. Rotenberg, E . Crumlin)
- Nanyang Technological University (M. Srinvasan)
- University College London (P. Shearing. J. Franklin)
- University of California, Berkeley
- Umicore, Farasis Energy, Inc.

Responses to 2017 Reviewers Comments

1. *"The project is well focused and is part of larger efforts involving sophisticated characterization methods of interfacial materials and phenomena; The approach is well designed to answer the difficult questions about the reactions on the surface of active cathode materials; The project includes well -organized use of state-of-the-art with electrochemical methods. The project achieves success on shedding light on mechanisms of interfacial phenomena and surface reconstruction effects on impedances. Results can be integrated with others developing ALD to coat NMC to get a stable NMC Li-ion cell."*

We would like to thank Reviewers for their positive comments and encouragement.

2. *"The progress in this period has been very good; LBNL group has done a great job in investigating the effect of surface reconstruction in NMC electrodes; identification of surface reactivity, film formation, and surface reconstruction at the cathode and electrolyte interface are definite accomplishments of this project. It would be good to link the characterized interfacial phenomena to achieving kinetic control of the cathode reactivity. need to be extended to other Ni-rich NMC s besides the 5:3:2."*

We think that our characterization results can be extended to the whole class of NMC materials, including materials with higher Ni content. We do agree that this work should be extended to other cathode compositions. To be able to do it effectively we are developing PLD-based methodology to be able to produce NMC thin-film model electrodes of various chemical compositions.

3. *"The project has a large and strong collaboration; …this group up has wide collaborations with other institutes; …the project is well integrated with others at LBNL, but there is some degree of duplication with Doeff's presentation; collaboration with other academic institutions is excellent, …collaboration with industry could be improved."*

We strongly believe that our work is not duplicative to Doeff's efforts, in fact it supplement it very nicely with new data and provides a new interpretation of the of the effect of the surface Me(II) reconstruction layer, which is contrary to the commonly accepted view. We do agree that collaboration with industry can be improved. However, the focus and goal of this study is to provide a better understanding of basic phenomena in Li-ion systems, which may appear somewhat distant from the industry interests. On the other hand, we offer this knowledge and actively deploy it in collaborations with battery companies under ongoing USABC programs.

4. *"the group has a well-defined plan for future work; the proposed future research seems to be well organized and focused on the study of the reactions in a more localized way, implying the development of new experimental techniques, it should be good to try with another Ni -rich concentration to check if similar or even better behavior using the artificial reconstruction layer is obtained, establish intense collaborations with a theoretical-computational multi-scale team able to interact and provide feedback to the experimental approach from the atomistic to the mesoscopic scales; the proposed future work is very general; More emphasis on the dynamic aspects of the interfacial phenomena is needed in order to achieve the objective of kinetic control. More specific plans should be indicated."*

We would like to thank Reviewers for these valuable suggestions, which are particularly important in the mid- and long-term perspective of this project. We'll keep reaching out to our partners for help and assistance as well as we'll extend these studies to other cathode materials.

5. *"…study of these interfaces is vital to proposing solutions to eliminate or considerably reduce obstacles to developing a high-energy density battery; the project aims to improve the inadequate LIB energy and power density and calendar and cycle lifetimes for PHEV and EV applications; understanding of cathode operation and fading is of vital importance."*

We share the same opinion on the matter.

6. *"The team has adequate resource to achieve their goals; the resources appear reasonable; 440,000 per year directly support ing the group seems sufficient although no number of supported researchers is reported."*

The current funding level is sufficient to support 0.3 FTE of the PI and 1 postdoc. We believe that the presented scope of work and the corresponding results meets or exceed the expectations, which are adequate for the current funding level.

Critical Assumptions and Issues - none